

PATENT SPECIFICATION

(11) 1 226 234

1 226 234

NO DRAWINGS

- (21) Application No. 7854/69 (22) Filed 13 Feb. 1969
 (45) Complete Specification published 24 March 1971
 (51) International Classification C 08 f 37/00
 (52) Index at acceptance
 C3P 12C 12D1 3C13B 3C6A 3C6B 7C13B 7C6A 7C6B
 7D1A 7D1X 7D2B 7D3 7D8 7K2 7K7
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(54) RESINOUS COMPOSITIONS

- (71) We, SHELL INTERNATIONALE RE-
 SEARCH MAATSCHAPPIJ N.V., a company or-
 ganised under the laws of The Netherlands,
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 Netherlands, do hereby declare the invention,
 for which we pray that a patent may be grant-
 ed to us, and the method by which it is to
 be performed, to be particularly described in
 and by the following statement:—
 This invention relates to a resinous composi-
 tion comprising a resin component and a poly-
 meric component. The invention also relates
 to a mixture suitable for application in road
 building. The invention further relates to cut-
 backs suitable for application in road building
 and to cutbacks suitable for industrial applica-
 tions. Furthermore the invention relates to a
 process for the preparation of the said resinous
 compositions.
 The quantitative differences between the
 properties of resins and non-resinous polymeric
 substances can not easily and clearly be defined
 although qualitative differences are readily ap-
 parent to those skilled in the art. However,
 the properties of resins are discussed in general
 terms on pages 11 and 12 of "The Chemistry
 of Synthetic Resins" Volume 1 by C. Ellis,
 published by Reinhold Publishing Corporation
 1935. The term resin as used herein does not
 include polymers of vinyl aromatic or vinyli-
 dene aromatic compounds.
 As a result of increasing demands of modern
 traffic there is a growing interest in road sur-
 faces which possess a certain colour, for exam-
 ple yellow, brown or red. It is known that
 resinous compositions, being light-coloured
 themselves, are very suitable as binder material
 in coloured surfaces. The desired colour may
 be obtained by making a choice out of the
 many available pigments.
 Resins, when applied as binders in road-
 building and industrial fields, often have the
 disadvantage that the binder does not com-
 pletely meet the requirements. This disadvan-
 tage, which will make itself more strongly felt

as the requirements to be met by the binder
 are more stringent, is often due to the unsatis-
 factory rheological properties of the binder.
 Some examples from the practice of road-
 building may serve to illustrate the above.
 In regions with extremely high temperatures
 in summer and extremely low temperatures in
 winter it is, for road-building applications, de-
 sirable to have resins possessing both an ade-
 quate resistance to plastic deformation at very
 high road temperatures and an adequate plasti-
 city at very low temperatures. This combina-
 tion of properties is generally not found in
 resins.
 For application in regions with a milder cli-
 mate, too, there is a distinct need of resinous
 binders having a higher resistance to plastic
 deformation than the resinous binders available
 at the moment.
 In the past it has proved impossible to pre-
 pare, by the conventional techniques, of pre-
 paration, resins or resin-oil mixtures that
 offered a satisfactory solution to the problems
 mentioned above.
 In fact, an improved resistance to plastic
 deformation can be obtained by application of
 harder resinous binders, but this involves a de-
 crease in plasticity at low temperatures and
 an increase in viscosity at temperatures that
 are generally applied in the preparation of
 mixtures of the resinous compositions with
 mineral aggregate. Conversely, the application
 of softer resinous binders will improve the
 plasticity at low temperatures but has the dis-
 advantage of too strong a production of the
 resistance to plastic deformation at high road
 temperatures.
 In the past it has already been suggested
 that the rheological properties of resins or
 resin/oil mixtures be improved by the addition
 of polymers. Rubbers, such as natural rubbers
 and synthetic rubbers, have proved very suit-
 able for this purpose. It has been found that
 the addition of such rubbers to resins or
 resin/oil mixtures may exert a favourable

influence on both the low-temperature brittleness and the resistance to flow at high road temperatures. A disadvantage of applying these rubbers is, however, that although they are very effective for the purpose in question when vulcanized, they can only be finely dispersed into a resin or a resin/oil mixture in the non-vulcanized state. Consequently, for the desired effect to be obtained, rather high concentrations of unvulcanized rubber with a relatively high molecular weight must be applied, which generally results in the viscosities at the processing temperatures being increased too much.

It has been found that these disadvantages can largely be overcome by applying a class of thermoplastic rubbers that have recently become available.

The invention provides a resinous composition comprising:—

(a) 85 to 99% by weight, based on weight of resinous composition, of thermoplastic material having an aromaticity (as hereinafter defined) of more than 0.28 and consisting of a resin or a stable resin-oil mixture, said resin not being a polymer of a vinyl aromatic or vinylidene aromatic compound and

(b) 1 to 15% by weight, based on weight of resinous composition, of a block copolymer having the general formula: A—B—A, in which the two A's represent identical or different thermoplastic, non-elastomeric blocks derived from a monovinyl aromatic compound and in which B represents an elastomeric polymer block derived from a conjugated diene, said elastomeric polymer block B being optionally partially or fully hydrogenated.

The term '% by weight' is represented sometimes hereinafter by the term '% w'.

For brevity, thermoplastic rubbers of the aforesaid type are defined in this patent application as "block copolymers". At room temperature these block copolymers have the properties of a vulcanized rubber. At temperatures above 70°C the vulcanised character disappears, which renders these block copolymers excellently suitable for dispersion in molten resin or a molten resin-oil mixture. Upon these mixtures being cooled down, the vulcanized character of the block copolymers reappears and very elastic, rubber-like products are obtained. In this way mixtures can be obtained with an excellent resistance to flow at high road temperatures, while owing to the thermoplastic character of the block copolymer only a slight increase in processing temperature is required. Furthermore, by starting from soft resins or resin-oil mixtures, and applying these block copolymers, mixtures can be obtained which, in addition to the aforesaid favourable properties, have a very low brittleness temperature. Application of these block copolymers thus offers the possibility of considerably widening the viscoelastic temperature range of resinous binders.

Mixtures comprising more than 85% by weight but not more than 99% by weight, based on weight of mixture, of a resin or a resin-oil mixture and less than 15% by weight but not less than 1% by weight, based on weight of mixture, of a block copolymer are all sufficiently workable to be applied by the current techniques used in conventional road building and the industrial field. Generally, the temperatures required for application are below the temperatures where there is a chance of thermal and/or oxidative decomposition of resins or polymers. It has been found, however, that not all resinous compositions are sufficiently stable upon prolonged storage at a temperature of about 140°C. For the sake of brevity, the term "storage stability" will be used hereinafter to denote the stability during storage under nitrogen at a temperature of about 140°C for nine days. Mixtures having insufficient storage stability separate into a resin-or-resin oil-rich phase hardly containing any polymer and a polymer-rich phase in which only a small quantity of resin or resin-oil mixture is present. The insufficient storage stability of some of these mixtures is a serious impediment to their practical application, the more so since these storage-unstable mixtures often display bleeding phenomena at room temperature, which result in poor adhesion of the binder to mineral aggregate.

It has further been found that upon the above-mentioned storage-unstable mixtures being diluted with volatile organic solvents, rapid phase separation often occurs at room temperature.

Microscopic examination of a great number of mixtures of block copolymers with different resins or resin-oil mixtures, using a magnification of 250 times, revealed that all these mixtures could be divided into any one of the following three classes:

- (1) heterogeneous;
- (2) microdisperse;
- (3) homogeneous.

Furthermore, it was found that only those mixtures which on the basis of microscopic examination could be placed in either class (2) or class (3) displayed satisfactory storage stability. In addition, it was found that in most cases it was possible to prepare from the mixtures that could be placed in class (2) or (3), by dilution with volatile organic solvents, cutbacks which displayed no phase separation at room temperature.

The applicant has found that the aromaticity of the resin or the resin-oil mixture plays an important role in this context. For, it has been found that the aromaticity of the resins or resin-oil mixtures in microdisperse and homogeneous resinous compositions is more than 0.28 and that of the resins or resin-oil mixtures in heterogeneous resinous compositions is 0.28 or lower than 0.28. The word "aromaticity" is used in this patent application

to denote the fraction of the carbon atoms which is present in aromatic rings.

Closer examination of mixtures comprising more than 85%w but not more than 99%w of a resin or a resin-oil mixture and less than 15%w but not less than 1%w of block copolymer revealed that mixtures in which the aromaticity is higher than 0.28 possess sufficient storage stability. The percentages are based on the weight of the mixtures. Mixtures for which the aromaticity is lower than 0.28 appear to have insufficient storage stability. This often means in addition that, if a mixture having an aromaticity higher than 0.28 is diluted with a volatile organic solvent, no demixing will occur at room temperature.

In addition to the importance of the aromaticity of resins or resin-oil mixtures for the storage stability of mixtures of these resins or resin-oil mixtures with block copolymers, investigations also revealed that the aromaticity exerts a major influence on the rheological properties of the mixtures. Thus it was found that the increase in Ring and Ball temperature such as occurs upon addition of block copolymers to resins or resin-oil mixtures was smaller according as the resin or resin-oil mixture possessed a higher aromaticity. The best results as to improvement of the flow properties at high temperature are obtained when mixtures are prepared which on account of their microscopic picture can be placed in the microdisperse class. It has also been found that the aromaticity of the resins or resin-oil mixtures in microdisperse resinous compositions is more than 0.28 but less than 0.31 and that of homogeneous mixtures is 0.31 or larger. Resinous compositions in which the aromaticity of the resin or resin-oil component is lower than 0.31 but more than 0.28 are very suitable.

One of the major components of the composition of the invention is a resin. However, the term resin as used herein does not include polymers of vinyl aromatic or vinylidene aromatic compounds. A great variety of resins may be used provided they can exist in the liquid state without or substantially without suffering from decomposition. Natural and synthetic resins may be used. Formation of natural resins occurs in the tree as a result of injury to the bark; a viscous liquid pours out of the wound. Many natural resins are transparent and/or translucent, they have a certain brittleness and show a conchoidal fracture. Their colour can be from practically water-white to yellow and brown. The resins may be used as such or may have been subjected to processes such as fusing, sweating, melting or cracking. Examples of suitable natural resins are rosin-type resins, Congo copal, Kauri copal and shellac. Rosin-type resins, being solid resinous material obtained from the oleoresin or stump wood of pine trees are very suitable. Examples of rosin-type resins are gum rosin, wood rosin and tall oil rosin. These resins may be present

unmodified or modified by treatments, such as for example hydrogenation, disproportionation or polymerization. Examples of suitable rosin-based resins are: wood rosin, polymerized rosin, hydrogenated rosin, disproportionated rosin, dimerized rosin, pentaerythritol esters of rosin, pentaerythritol esters of hydrogenated rosin, pentaerythritol esters of polymerized rosin, glycerol esters of rosin, glycerol esters of hydrogenated rosin, methyl esters of hydrogenated rosin. The words "hydrogenated rosins" in the above list include both fully and partially hydrogenated rosins. The polymerized rosins may be in any of the usually commercially available stages of polymerization.

A great variety of synthetic resins may be used. Hydrocarbon resins are preferred. They may be prepared by polymerization of unsaturated hydrocarbons, either catalytically or thermally and under controlled conditions to yield resins of a desired average molecular size depending on the required melting point. Being polymers of hydrocarbons only, their behaviour is essentially that of a hydrocarbon. These resins contain essentially no esters and are not saponifiable. They are unaffected by moderate concentrations of acids, alkalis or salts. They are quite soluble in aromatic hydrocarbons and in most petroleum diluents. These resins have extensively been discussed in the literature.

The resin may have been produced by polymerization of one or more unsaturated hydrocarbons present in an unsaturated petroleum fraction. As examples of useful unsaturated petroleum fractions may be mentioned thermally cracked stocks and unsaturated hydrocarbons obtained in pyrolysis of hydrocarbons which are gaseous at normal pressure and temperature.

The resin may also have been produced by polymerization of one or more unsaturated hydrocarbons present in a coal tar distillate. Coumarone-indene resins have proved to be very suitable.

Terpene-phenolic resins are also suitable for use in the resinous composition of the invention. The word "Terpene" used herein relates to terpenes in the restricted sense of the word and such non-ionic oxygen-free or oxygen-containing saturated or unsaturated compounds immediately derived therefrom. Hydrocarbons such as limonene, pinene, camphene as well as sesquiterpenes and di- or polyterpenes may be used. They may be derived primarily from natural sources such as turpentine, conifer oils and other well-known sources of terpenes. They may be condensed with phenols by any suitable method.

If desired, a mixture of resins may also be used. For example, a mixture of petroleum resins and coal tar resins, or mixture of a natural and a synthetic resin may be used.

The resin may be used in the absence of an oil. Usually, however, the resin is used in

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admixture with an oil, the oil having the chief advantage of substantially reducing the cost of the resinous composition without any material degradation in other properties thereof. Any suitable oil may be used, provided the resin-oil mixture used is stable. The mixture is stable if it does not separate into its components at the temperature at which it is mixed with the block copolymer and does not suffer from exudation or phase separation at the service temperature of the resinous composition. The fact whether stable mixtures can be prepared from a particular resin and a particular oil can easily be determined experimentally.

The aromaticities of a particular resin and a particular oil play an important role in connection with the stability of a mixture of that resin and that oil. For example, mixtures of an aromatic resin and a paraffinic oil are generally only then stable if such mixtures have only a low content of the paraffinic oil. Higher oil contents are allowed if the oils are more aromatic. Therefore, aromatic resins are usually employed in admixture with aromatic oils. Mixtures of a paraffinic resin and an aromatic oil are generally only then stable if such mixtures have only a low content of the aromatic oil. Paraffinic oils, however, may be present in larger proportions in admixture with paraffinic resins. Therefore, paraffinic resins are usually employed in admixture with paraffinic oils. In view of the above it is preferred that the aromaticities of the resin and the oil be of the same order of magnitude. As in many cases the available resins are aromatic, aromatic oils are usually applied to prepare stable resin-oil mixtures.

The block copolymers of which in the preparation of the compositions in question less than 15%w but not less than 1%w should be mixed with more than 85%w but not more than 99%w of a resin or a resin-oil mixture, have the general formula $A - B - A$, in which A and B have the meaning mentioned hereinbefore. The percentages are based on the weight of the compositions. Preferably, the thermoplastic non-elastomeric blocks A have a molecular weight between 7,500 and 100,000, particularly between 10,000 and 50,000. Preferably, the elastomeric polymer block B has a molecular weight between 25,000 and 1,000,000, particularly between 35,000 and 150,000. Preferably, the thermoplastic polymer blocks A are present in the block copolymer in a quantity from 10 to 70%w, particularly from 20 to 50%w, based on weight of copolymer. As monovinyl aromatics suitable for the preparation of the thermoplastic polymer blocks in the block copolymers in question may be mentioned styrene and α -methylstyrene. As conjugated dienes suitable for the preparation of the elastomeric polymer blocks in the block copolymers in question preferably dienes with four to eight carbon atoms

per molecule are selected, particularly butadiene and isoprene.

Examples of suitable block copolymers are polystyrene-polyisoprene-polystyrene and polystyrene-polybutadiene-polystyrene. Preference is given to the application of a polystyrene-polybutadiene-polystyrene block copolymer as polymeric component in the preparation of the composition according to the invention.

The quantity in which said block copolymers are applied is to a large extent determined by the field of application. For applications in road building, generally quantities are chosen which lie between 1 and 10 %w and in particular between 1 and 5%w based on weight of mixture applied. Moreover, for applications in road building preference is given to resinous compositions in which the resin or alternatively, the resin-oil mixture has a penetration between 50 and 500 at 25°C. For application in road building it is customary to mix the resinous composition with graded material i.e. inorganic particulate filler material of suitable size, for example, mineral aggregate, which is preferred. Generally, for applications in road building, mixtures are considered comprising 3 to 45%w, based on weight of mixture, of the resinous compositions according to the invention and 85 to 97%w, based on weight of mixture, of graded material. Optionally, pigments of any desired colour may be present in the resinous compositions.

It is also possible to apply the resinous compositions in question for road-building purposes in the form of cutbacks. In that case preference is given to cutbacks comprising between 70%w and 90%w, based on weight of cutback, of the resinous composition in question and between 10%w and 30%w, based on weight of cutback, of a volatile organic solvent containing more than 30% by volume, based on volume of organic solvent, aromatic compounds.

If it is the intention to apply the resinous compositions in the industrial field, for example as adhesive or as primer for pipe coatings, preferably compositions are selected comprising between 5%w and 15%w, based on weight of composition, of the block copolymers. Moreover, for industrial applications preference is given to compositions whose resin or alternatively, resin-oil mixture has a penetration at 25°C between 10 and 1000. If it is the intention to apply the resinous compositions in question in the industrial field in the form of cutbacks, preferably cutbacks are selected comprising between 40%w and 70%w, based on weight of cutback, of the resinous composition in question and between 30%w and 60%w, based on weight of cutback, of a volatile organic solvent containing more than 30% by volume based on volume of organic solvent aromatic compounds.

- The preparation of the compositions may be effected in a simple manner by stirring the polymeric component as a finely divided, solid substance or in the form of a solution, for instance, in benzene or toluene, into the molten resin or resin-oil mixture. The solvent may afterwards be removed through evaporation. The invention, accordingly, also relates to a process for the preparation of resinous compositions by mixing 85 to 99% by weight, based on weight of resinous composition, of a thermoplastic material having an aromaticity of more than 0.28 and consisting of a resin or a stable resin-oil mixture, said resin not being a polymer of a vinyl aromatic or vinylidene aromatic compound, with 1 to 15% by weight, based on weight of resinous composition, of a block copolymer having the general formula: A — B — A, in which the two A's represent identical or different thermoplastic, non-elastomeric blocks derived from a monovinyl aromatic compound and in which B represents an elastomeric polymer block derived from a conjugated diene, said elastomeric polymer block being optionally partially or fully hydrogenated.
- The invention will now be elucidated with the aid of the following Examples.
- A number of resinous compositions were prepared of which the resin-oil mixtures had been made from resins having the properties shown in Table I.

TABLE I

Resin No.	Origin of the resin	Penetration at 25°C. 0.1 mm	Softening point Ring and Ball, °C	f _a
R1	coal tar	less than 1	145	0.72
R2	petroleum	less than 1	150	0.50

- R1 was a coumarone-indene resin prepared by polymerization of an unsaturated coal tar fraction boiling between 150° and 200°C; resin R2 was prepared by polymerization of unsaturated petroleum hydrocarbons.
- The properties mentioned in the table above and elsewhere in this patent application, viz. penetration at 25°C., softening point Ring and Ball and aromaticity (indicated by f_a) were determined as follows:
- penetration at 25°C... ASTM D 5
softening point Ring and Ball ... ASTM D 36
- The f_a was calculated from the density 20/4°C, the percentage carbon and the percentage hydrogen according to a method described by R. B. Williams in Proceedings, 6th World Petroleum Congress, section IV, paper 17 (1963).
- A few properties of the oils used are shown in Table II.

TABLE II

Oil No.	Viscosity, cS, at			f _a
	25°C.	60°C.	100°C.	
F1	165	27	8	0
F2	3600	133	17	0.45

- Oil F1 is a vacuum distillate from which the aromatics had been extracted. Oil F2 is an aromatic extract obtained by solvent extraction of a deasphaltenized vacuum residue.
- Thirteen resinous compositions were prepared by mixing a resin-oil mixture with a quantity of block copolymer. As block copolymer in these cases a polystyrene - polybutadiene - polystyrene block copolymer having a molecular weight of 14,000 — 65,000 — 14,000 was applied. To seven other resinous compositions no polymer was added and a further two resinous compositions were mixed with a rubber instead of with a block copolymer. A few properties of the resinous compositions prepared and presented in Table III. The percentages by weight of the block copolymer content are based on the weight of the resinous compositions. The percentages by weight of the resin-oil mixture components are based on the weight of the resin-oil mixture. The percentages by weight of the F¹-content in oil are based on the weight of the oil.

TABLE III

Ex. No.	Composition of resin-oil mixture				stability of resin-oil mixture + = stable - = unstable	f_a of the resin-oil mixture	block co-polymer content, %w	properties of the compositions		
	R1 %w	R2 %w	oil %w	F1-content in oil, %w				penetration at 25°C, 0.1 mm	softening point Ring and Ball °C.	viscosity at 60°C, poise
1	39	0	61	0	+	0.55	0	90	39	—
2	38	0	62	0	+	0.55	5	90	42	—
3	32	0	68	45	—	0.40	5	80	51	300
4	38	0	62	60	—	0.36	5	90	68	—
5	0	42	58	0	+	0.45	0	90	42	—
6	0	42	58	0	+	0.45	5	90	46	—
7	0	53	47	50	+	0.36	0	90	43	—
8	0	52	48	50	+	0.36	5	90	48	—
9	0	57	43	80	+	0.33	0	90	44	—
10	0	56	44	80	+	0.33	5	90	55	—
11	0	58	42	100	—	0.30	0	90	46	—
12	0	57	43	100	—	0.30	5	90	61	—
13	0	58	42	50	+	0.38	0	34	52	—
14	0	58	42	0	+	0.47	0	5	61	—
15	0	53	47	50	+	0.37	5	84	49	2000
16	composition of example 15 after Rolling Thin Film Oven Test				+	0.37	5	76	47	1700
17	a commercial product containing rubber				+	0.30	5	79	46	1700
18	the commercial product after Rolling Thin Film Oven Test				+	0.30	5	57.5	46.5	1200
19	0	50	50	80	+	0.30	5	190	51	—
20	0	48	52	80	+	0.29	10	190	58	—
21	0	60	40	80	+	0.34	10	25	75	—
22	0	40	60	80	+	0.26	5	450	48	—

- 1) Compositions not according to the invention as they do not contain block copolymer and/or are based on unstable resin-oil mixtures and/or have too low an f_a .
- 2) Compositions according to the invention but not complying with the specification for the softening point Ring and Ball for a conventional road building bitumen of the pertaining penetration.
- 3) Compositions according to the invention and complying with the specification for the softening point Ring and Ball and penetration for a conventional road building bitumen.

Table III shows that mixtures of coumarone-indene resin R1 and oils containing 45 and 60%w based on weights of oil, of the paraffinic oil F1 are unstable (compare Examples 3 and 4). It was furthermore found (but not shown in Table III) that mixtures of resin R1 and oils containing up to 20%w of oil F1, based on weight of oil, are stable. On the other hand, mixtures of resin R1 with about 60%w of the aromatic oil F2, based on weight of oil are stable (compare Examples 1 and 2). From Examples 1 — 4 it follows that a very aromatic resin is preferably mixed with an aromatic oil for the preparation of stable resin-oil mixtures. This very aromatic resin-oil mixture causes a slight increase in softening point Ring and Ball upon addition of block copolymer (compare Examples 1 and 2).

The petroleum resin R2 (which is much less aromatic than resin R1) may be mixed with oil containing up to 80%w of the paraffinic oil F1, based on weight of oil (compare Examples 5—12).

Comparison of the softening points and aromaticities of the resinous compositions prepared in Examples 6, 8 and 10 shows that the softening point of 80/100 penetration mixtures containing 5%w block copolymer, based on weight of mixture, increases according as the aromaticity of the resin-oil mixture decreases, notwithstanding the very low viscosity

of the oil F1 (165cS at 25°C compared with 3600 cS at 25°C for oil F2). From the softening points found in Examples 9, 13 and 14 it follows that the softening point decreases according as the content of oil F1 increases, no block copolymer being present.

Composition 17 was prepared using a commercial product instead of the block copolymer of the invention. This commercial product was a resin-oil mixture containing 5%w of styrene-butadiene rubber, based on weight of mixture. Comparison of the results of this commercial product with one of the resinous compositions according to the invention shows that about the same softening point and the same viscosity at 60°C are obtained. The block-copolymer containing mixtures however, are considerably more rubber elastic (see Examples 6 and 17) and are (compare Examples 16 and 18) more resistant to aging during mixing with mineral aggregate. This aging is simulated in the Rolling Thin Film Oven Test as described in Californian Test Method 346 — C of the Department of Public Works, Division of Highways (State of California).

Examples 19 — 21 show that it is possible to prepare light-coloured binders of other grades than the 80/100 penetration grade and which comply with the specification for the softening point. A few requirements for conventional road building bitumens are shown in Table IV.

TABLE IV

Grade	penetration at 25°C. 0.1 mm	softening point Ring and Ball, °C.	viscosity at 60°C, poise
180/200 pen	190	>37	>1500
80/100 pen	90	>45	
20/30 pen	25	>59	

The composition of Example 22 was not storage-stable, the aromaticity of the resin-oil mixture being below 0.28.

WHAT WE CLAIM IS:—

1. A resinous composition comprising:
 - (a) 85 to 99%, by weight, based on weight of resinous composition, of a thermoplastic material having an aromaticity (as hereinbefore defined) of more than 0.28 and consisting of a resin or a stable resin-oil mixture, said resin not being a polymer of a vinyl aromatic or vinylidene aromatic compound and
 - (b) 1 to 15%, by weight, based on weight of resinous composition, of a block copolymer having the general formula A—B—A, in which the two A's represent identical or different thermoplastic, non-elastomeric blocks

derived from a monovinyl aromatic compound and in which B represents an elastomeric polymer block derived from a conjugated diene, said elastomeric polymer block B being optionally partially or fully hydrogenated.

2. A resinous composition as claimed in claim 1, in which the resin is a hydrocarbon resin.

3. A resinous composition as claimed in claim 2, in which the resin has been produced by polymerization of one or more unsaturated hydrocarbons present in an unsaturated petroleum fraction.

4. A resinous composition as claimed in claim 2, in which the resin has been produced by polymerization of one or more unsaturated hydrocarbons present in a coal tar distillate.

5. resinous composition as claimed in claim 4, in which the resin is a coumarone-indene resin.
6. A resinous composition as claimed in any of the preceding claims, in which the thermoplastic, non-elastomeric blocks A have a molecular weight from 7,500 to 100,000, particularly from 10,000 to 50,000.
7. A resinous composition is claimed in any one of the preceding claims, in which the elastomeric polymer block B has a molecular weight from 25,000 to 1,000,000, particularly from 35,000 to 150,000.
8. A resinous composition as claimed in any one of the preceding claims, in which the thermoplastic polymer blocks A are present in the block copolymers in a quantity from 10 to 70% by weight, based on weight of block copolymer, particularly from 20 to 50% by weight, based on weight of block copolymer.
9. A resinous composition as claimed in any one of the preceding claims, in which the block copolymer is a polystyrene-polybutadiene-polystyrene block copolymer.
10. A mixture suitable for application in road buildings, comprising 3 to 15% by weight, based on weight of mixture, of a resinous composition as claimed in any one of the preceding claims and 85 to 97% by weight, based on weight of mixture, of graded material (as hereinbefore defined).
11. A mixture as claimed in claim 10, in which the resinous composition contains the block copolymer in a quantity of less than 10% by weight, based on weight of resinous composition.
12. A mixture as claimed in claim 10 or 11, in which the resin or the resin-oil mixture in the resinous composition has a penetration at 25°C between 50 and 500. (Determined according to ASTM D5).
13. A mixture as claimed in any one of claims 10 to 12 comprising a pigment.
14. Cutbacks suitable for application in road building, comprising between 70% and 90% by weight, based on weight of cutback, of a resinous composition as claimed in any one of claims 1 to 8 and between 10% and 30% by weight, based on weight of cutback, of a volatile organic solvent with a content of aromatic compounds higher than 30% by volume, based on volume of organic solvent.
15. Cutbacks as claimed in claim 14, in which the quantity of the block copolymer in the resinous composition is less than 10% by weight, based on weight of resinous composition.
16. Cutbacks as claimed in claim 14 or 15, in which the resin or the resin-oil mixture in the resinous composition has a penetration at 25°C between 50 and 500. (Determined according to ASTM D5).
17. Cutbacks suitable for industrial applications, comprising between 40% and 70% by weight, based on weight of cutback, of a resinous composition as claimed in any one of claims 1 to 9 and between 30% and 60% by weight, based on weight of cutback, of a volatile organic solvent with a content of aromatic compounds higher than 30% by volume, based on volume of organic solvent.
18. Cutbacks as claimed in claim 17, in which the quantity of the block copolymer in the resinous composition is between 5% and 15% by weight, based on weight of resinous composition.
19. Cutbacks as claimed in claim 17 or 18, in which the resin or the resin-oil mixture in the resinous composition has a penetration of 25°C between 10 and 100 (Determined according to ASTM D5).
20. Resinous compositions, mixtures for road building application and cutbacks, substantially as hereinbefore described, with particular reference to the examples 2, 6, 8, 10, 15, 19, 20 and 21.
21. A process for the preparation of a resinous composition by mixing 85 to 99% by weight, based on weight of resinous compositions, of a thermoplastic material having an aromaticity (as hereinbefore defined) of more than 0.28 and consisting of a resin or a stable resin-oil mixture, said resin not being a polymer of a vinyl aromatic or vinylidene aromatic compound with 1 to 15% by weight, based on weight of resinous composition, of a block copolymer, having the general formula: A — B—A, in which the two A's represent identical or different thermoplastic, non-elastomeric blocks derived from a monovinyl aromatic compound and in which B represents an elastomeric polymer block derived from a conjugated diene, said elastomeric polymer block B being optionally partially or fully hydrogenated.
22. A process for the preparation of resinous compositions, mixtures for road building application, and cutbacks, substantially as hereinbefore described, with particular reference to the Examples 2, 6, 8, 10, 15, 19, 20 and 21.

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